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(54) Title: SURFACE TREATMENT OF AN OBJECT

(57) Abstract

A method of treating an object involving directly applying, e.g. printing, masking material to a surface, e.g. a metallic surface, of the object to provide a desired pattern of masked and unmasked areas and treating the partially masked surface, e.g. by etching, to remove material, e.g. metallic material, from the unmasked areas. The masking material is preferably applied under computer control by an ink-jet printing head. The etching may suitably comprise chemical etching, electro-chemical etching or pulsed electro-chemical etching.

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Surface Treatment of an Object

Technical field

This invention relates to a method of treating an object by selectively removing material from at least one part of a surface, preferably a metallic surface, of the object, the method being of the kind comprising partially masking said object surface with masking material to provide a desired pattern of masked and unmasked surface areas and treating the partially masked surface to remove material from the or each unmasked area, the or each masked area acting as a barrier to prevent said treating being effective to remove material from the object surface underlying the masked area. In particular, but not exclusively, the invention relates to a method of etching a desired surface pattern onto an object which may not be of even geometry in all axes. Typically, for example, the invention finds application in applying a desired surface finish to a steel roller of a rolling mill, in applying wording, logos, bar codes or the like to flat, curved or other non-linear metallic surfaces or in the manufacture of printed circuit boards.

Background Art

In order to impart a desired surface finish or texture to steel sheets, e.g. for use in vehicle panels, it is known to provide rollers in the final temper rolling stage of a cold strip mill with a surface texture. The finish imparted by such surface textured rollers to the sheet steel may influence the painted appearance, coating adhesion and formability of the sheet steel.

At present there are four known techniques for surface texturing a roller. The traditional process is shot blast texturing (SBT). This involves firing particles of aluminium oxide or other hard material at the surface of the roller. However, this leads to limitations in the hardness

of the roller as it must be softer than the shot being used to texture it. It also suffers by being difficult to accurately control, resulting in wide variations of peak height and a poor bearing ratio. This combined with the hardness limitation also reduces the wearability and thus the service life of the roller.

The SBT technique for surface texturing a roller has been widely replaced by the more recent processes of electrical discharge texturing (EDT), laser texturing (LT) and electron beam texturing (EBT). All these processes offer greater control than SBT and are effectively independent of roller hardness. The EDT approach is based on the well established process of electro-discharge machining. The roller is mounted on a lathe, grinding machine or the like, and is rotated at a constant velocity while the tool electrode is traversed along its length at constant rate on a zero backlash servo system. A dielectric fluid such as paraffin flows between the tool and the roller. This breaks down when a suitable voltage is applied across the electrodes, the resulting spark melting a small crater in the surface of the roll. By controlling the frequency, duration and current of the spark different surface roughnesses can be created.

The LT process uses a laser beam to remove material from the surface of the roller. The unfocussed beam is chopped by a rotating disk then focused into a spot, typically 0.1 mm diameter, on the roller surface. This causes the metal to first melt and then vaporise. When the beam is removed the surface cools leaving a pit. The rotation of the roller and the pulsing frequency of the beam set the spacing of the craters, and thus the peak count on the textured sheet. This produces a surface which has reportedly good pressing and painting performance, although there have been reports of the regular pattern of the texture causing diffraction patterns on the surface of the painted sheet.

EBT is similar to the LT process but uses an electron beam to provide a highly controllable energy source for material removal. Equipment costs appear to be high and the machining must take place in a vaccum.

The random processes, SBT and EDT, have a large waviness (λ > 0.8mm) component in their texture (particularly SBT) which has been linked to a reduction in image clarity of the painted sheet.

A known technique for treating generally flat metallic surfaces is the conventional etching process known as photochemical machining. This process involves coating the metallic surface of a workpiece with a light-sensitive chemical or photo-resist. A desired image is projected onto the surface to selectively expose the photo-resist coating. A developing solution is then used to strip or remove all areas to be exposed to a chemical etchant. However a disadvantage of this known process is that it is difficult to expose the required images onto a curved or non-flat surface. Also there are a number of process stages involved.

The present invention seeks to provide a novel and relatively simple method of treating an object by selectively removing material from the surface of the object. The invention involves a novel method of masking surfaces, e.g. metallic surfaces, which may be flat, cylindrical or of other non-planar form, in a surface treating process.

Disclosure of Invention

According to the present invention a method of the kind referred to is characterised in that the masking material is directly applied, e.g. printed, onto the object surface to provide said desired pattern of masked and unmasked surface areas.

The present invention finds particular, but not exclusive, application in applying a desired surface pattern to non-flat surfaces, preferably metallic surfaces. One particular application involves the surface texturing of rolls or rollers which themselves are intended to contact and surface treat or texture other articles. Such surface treated rollers may be used, for example, to coat, roll or press the other articles which may be metallic or non-metallic. Examples of articles which can be so treated are rolled steel, paper or plastic sheet, plated or painted components, overlaid plain bearings and the like. A metallic object may have its textured surface subsequently coated with ceramic or polymer material to give the object hard wearing or low friction surface properties beneficial when treating other articles. The invention may be applied to other surface treating or etching processes which involve the creation of a mask on a flat or non-flat, e.g. curved, object surface to be treated.
It may also be used to set spatial characteristics of the surface texture, e.g. roughness, waviness and form.

Preferably the masking material is printed onto the object surface under computer control to provide the said desired pattern of masked and unmasked surface areas. Different patterns of masked and unmasked surface areas can thus be produced under software control. A wide range of computer-controlled printing techniques can also be used to provide the desired pattern.

Preferably the masking material is applied to the object surface by a printing head of an ink jet printing device. By the use of computer control, the position of the printing head relative to the object surface can be accurately controlled. Conveniently the printing head has a nozzle diameter of less than 50 microns, e.g. 36 microns, and provides a dot frequency of up to 80 KHz. Typically the ink jet printing device has a resolution of at least 170 dots per inch. The masking material suitably comprises, for example, a solvent based ink or a hot melt type of ink.

Preferably the object to be treated has a metallic, e.g. a steel, surface. In this case the masking material may comprise a solvent based ink. The surface treating may comprise chemical etching using a suitable chemical etchant, e.g. ferric chloride solution, electro-chemical or pulsed electro-chemical etching. If pulsed electro-chemical etching is employed, both the crater depth and profile can be controlled by varying the pulse duration and current.

The treating of the partially masked surface may comprise photo-, electro-, chemical or laser machining or etching.

The method may be incorporated into a combined printing/treating (etching) system under computer control or otherwise although, alternatively, these process steps may be performed independently.

Brief Description of Drawings

Embodiments of the invention will now be described, by way of example only, with particular reference to the accompanying drawings, in which:

Figure 1 is a schematic view of apparatus for directly applying masking material onto a surface of a steel roller under computer control;

Figure 2 shows a plot depicting the surface profile of a section of a steel roller;

Figures 3 and 4 show plots depicting the surface profiles of a section of steel strip after and before, respectively, being rolled in a roll mill by a steel roller with a surface finish of the type depicted in Figure 2; and

Figures 4 and 5 show plots depicting fine and coarse surface textures of sections of conventionally

textured steel sheet.

Best Modes of Carrying Out the Invention

Figure 1 shows apparatus for carrying out a method of treating the surface of a steel roller 1. The roller 1 after treatment is intended to roll steel sheet in the final temper rolling stage of a cold strip mill (not shown) and typically may have a diameter of 300 mm and a length of 2 m. The surface treatment of the steel roller 1 is intended to provide a desired surface texture to the roller 1 so that a desired surface finish is imparted to steel sheet rolled by the roller 1 in a rolling mill. Such a surface finish may influence the painted appearance, coating adhesion and formability of the sheet steel.

The roller 1 is mounted for rotation about its longitudinal axis 2 in mounting means (not shown). The mounting means should be capable of rotating the roller 1 at a controllable set speed of rotation. A carrier 3 is mounted for traversing movement parallel to the axis 2 and carries an ink-jet print head 4 and a pulsed electro-chemical etching head 5. A control cable 6 is connected between the carrier 3 and a computer 7 for enabling the computer to control the operation of the print head 4, the operation of the etching head 5 and the traverse speed of the carrier 3. A further control cable 8 is schematically shown connected to the computer 7 for enabling the computer 7 to receive signals from means (not shown) sensing the speed of rotation of the roller 1 and for sending signals to control the speed of rotation of the roller 1 and/or the speed of printing of the print head 4.

In use, the carrier 3 traverses from one end A to the other end B of the roller 1 at a constant speed, typically of about 2 mm/s, as the roller 1 is rotated at a constant surface speed, typically of about 750 mm/s. The print head 4 directs ink-jet onto the cylindrical surface of the roller in a helical track to spray a desired ink pattern onto the

cylindrical surface of the roller. The ink sprayed onto the roller 1 rapidly dries and forms an etch-resistant mask on the cylindrical surface of the roller 1.

The electro-chemical etching head 5 is positioned behind the print head 4 as the carrier 3 traverses from end A to end B of the roller. The etchant from the etching head 5 is controllably applied to the cylindrical surface of the cylinder 1 bearing the now dry masking ink. Only those areas of the cylinder surface not covered by the masking ink are etched by the applied etchant. In this way a desired, etched or textured surface is formed on the roller 1.

The surface of the roller 1 may be cleaned to remove all traces of the etchant after a suitable time delay. If desired the metallic surface of the roller 1 may be coated to provide certain rolling enhancing properties. For example, the metallic surface may be coated with ceramic or polymer material to give a hard wearing or low friction textured roller surface.

In order to produce the desired masking pattern on the cylindrical surface of the roller 1 it is necessary to accurately control the speed of rotation of the cylinder 1 and the speed of traverse of the carrier 3 so that the helical path traced by the print head is able to cover the entire cylindrical roller surface without overlap. The print head 4 is controlled, preferably under software control 7, to apply or print a desired masking pattern directly onto the cylindrical surface of the roller 1. With software control, individual ink droplets from the ink jet or jets of the print head 4 can be deposited with high precision onto the cylindrical roller surface. The resolution of the printed mask is in effect dependent on the resolution of the print head. The intensity of the etching process can also be controlled by varying the pulse duration and current of the pulsed electro-chemical etching.

The masking ink suitably comprises a solvent based

ink, e.g. provided by Domino Printing Sciences PLC, although a hot melt type of ink could alternatively be used. Any suitable etchant can be employed, although the use of a pulsed electro-chemical etching technique enables relatively harmless etchants, e.g. sodium chloride, to be used.

The invention will now be further described with reference to the following non-limitative example.

EXAMPLE

In order to test a system to print and etch steel rollers, an experimental top roller for a rolling mill, having a length of 100 mm, a diameter of 52.5 mm and made from quench hardened EN31 bearing steel, was rotatably mounted on a lathe to rotate the roller at a constant velocity about the longitudinal axis of the roller. An ink-jet print head was mounted on the tool-post of the lathe so that the print head could traverse along the length of the roller.

The ink-jet printer employed was an Excel Hr ink-jet printer manufactured by Videojet. The machine is designed for contactless printing of items moving past the print head. The print head had a nozzle diameter of 36 microns and a dot frequency of up to 80 KHz. The stated resolution was 170 dots per inch. The ink applied to the roller was a solvent based ink provided by Videojet.

After a masking ink pattern was applied to the cylindrical surface of the roller under computer control, the still exposed surfaces (i.e. the unmasked surfaces) of the roller were treated with an etchant using conventional etching techniques. Ferric chloride solution was chosen as a readily available, effective etchant which is relatively harmless to work with. The roller was arranged with its longitudinal axis horizontal and with its lower cylindrical surface just touching the upper surface of a bath of the ferric chloride solution etchant. On rotation of the

roller, the cylindrical roller surface was refreshed with etchant on each revolution of the roller. The etching process used should be capable of:

(1) etching to the required depth without completely undercutting the mask; and

(2) maintaining the integrity of the ink mask for the duration of the etching process.

These factors may be influenced by etch time, etchant concentration, etch temperature, agitation/circulation of etchant, ink formulation and length of delay between mask printing and etching.

In order to compare the effectiveness of the process with known texturing techniques, reference is made to Figures 2 to 6.

Figure 2 illustrates a quench hardened EN31 bearing steel roller after being surface textured by the process described in the foregoing example. Figures 3 and 4 illustrate 50 mm wide, 1 mm thick steel strip after annealing which, in Figure 4, is depicted before being rolled in a temper mill and which, in Figure 3, is shown after being rolled in a temper mill, the upper roll of which is surface textured as shown in Figure 2. Figures 5 and 6 show samples of conventionally textured panel steel provided, respectively, with a fine textured finish and a coarse textured finish. In each case, the plot or trace was produced on a Zygo New View 100 non-contact 3-D surface measurement system and illustrates the surface profile, measured in microns, across a 3 mm section of the sample.

The textured roller finish shown in Figure 2 has a plateau type texture, giving a good bearing surface and consistent peak height. Crater depths are typically 8 ± 2 microns, with peak counts in the range of 30-40 peaks per cm. The pattern transferred well from the roller to the

annealed steel strip as can be seen in Figure 3. The map shows, however, a good consistency of valley depths even with the coarse texture (valley depths approximately 5-6 microns) shown here. This can be compared with the inconsistent nature of the original texture of the steel strip shown in Figure 4. Figures 5 and 6 show samples of conventionally textured steel, Figure 5 being a standard steel panel while Figure 6 is intended for deep drawing applications - hence the coarser, deeper texture. Neither of these conventionally textured steel panels exhibit the consistency of texture shown in Figure 3.

Although the invention has been described with respect to applying a desired surface texture to the cylindrical surface of a steel roller, e.g. for coating, rolling, pressing or otherwise treating articles, it will be appreciated that the invention has other applications. Indeed the invention is primarily concerned with applying or printing a desired pattern of masking material onto a flat or non-flat, e.g, curved, object surface, e.g. a metallic surface, to enable the unmasked part or parts of the surface to be etched or machined. The desired pattern of masked and unmasked surface areas is suitably produced by applying masking "ink" from a computer-controlled ink-jet printer. In this way the masking ink can be applied with high precision to produce the desired pattern.

Other areas where the invention can be employed are in the application of words, logos, bar codes or the like to metal surfaces and in the manufacture of printed circuit boards and photochemical machining. Although the ultimate resolution of photo-etching may be greater, the direct deposition method of the present invention offers the potential of providing quick in-house prototyping facilities at relatively low cost. An example of such an application would be a "desktop" printed circuit board prototyping unit which could accept standard output from an electronics CAD package to produce a board ready for etching within a few minutes. The etching can be performed in the same machine

as produced the masking. A further example would use the high speed combined mask and electrochemical etch process for on-line permanent product marking on production lines.

A method according to the present invention offers at least some of the following specific advantages:

1. Direct control of a print head as it lays a mask enabling an accurate, predetermined pattern of mask to be applied.

2. Software control of the surface pattern.

3. Application to a wide-range of computer-controlled printing techniques.

4. Adaptability to a range of flat and curved surface geometries.

5. Adaptability to a range of etch resistant media mask materials.

6. Adaptability to a range of chemical and electro-chemical etching techniques.

CLAIMS

1. A method of treating an object by selectively removing material from at least one part of a surface of the object, comprising partially masking said object surface with masking material to provide a desired pattern of masked and unmasked surface areas and treating the partially masked surface to remove material from the or each unmasked area, the or each masked area acting as a barrier to prevent said treating being effective to remove material from the object surface underlying the masked area, characterised in that the masking material is directly applied, e.g. printed, onto the object surface to provide said desired pattern of masked and unmasked surface areas.

2. A method according to claim 1, characterised in that the object surface is metallic and the said treating comprises removing metallic material from the unmasked area(s) of the metallic object surface.

3. A method according to claim 1 or 2, characterised in that the masking material is applied onto the object surface under computer control.

4. A method according to claim 1, 2 or 3, characterised in that the masking material is printed onto the object surface by an ink-jet printing head.

5. A method according to any of the preceding claims, characterised in that the object surface is not flat.

6. A method according to claim 5, characterised in that the treated object comprises a steel roller.

7. A method according to any of the preceding claims, characterised in that the material is removed from the unmasked area(s) of the object surface by etching or electro-chemical machining.

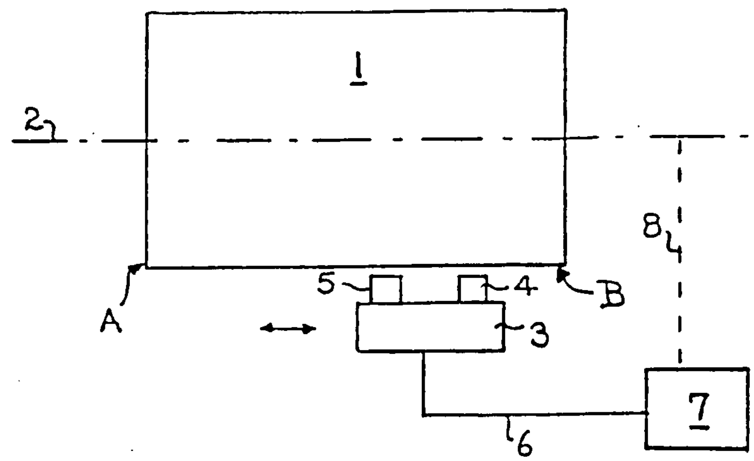
8. A method according to claim 7, characterised in that the etching comprises pulsed electro-chemical etching.

9. A method according to claim 8 when dependent on claim 4, characterised in that the printing head and an etching head are carried on a carrier which is moved relative to the object surface to directly apply the masking material from the print head and subsequently to apply etchant from the etching head to the masked and unmasked areas of the object surface.

10. A method according to claim 1, characterised in that the masking material comprises a solvent based ink or a hot melt type ink.

11. Apparatus for performing the method according to claim 1, characterised in that the apparatus includes an ink-jet printing head for applying masking ink directly to the object surface, computer control means for controlling the pattern of masked areas applied by the printing head to the object surface and etching means for removing material from unmasked areas of the object surface.

FIG. 1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6

FIG. 2

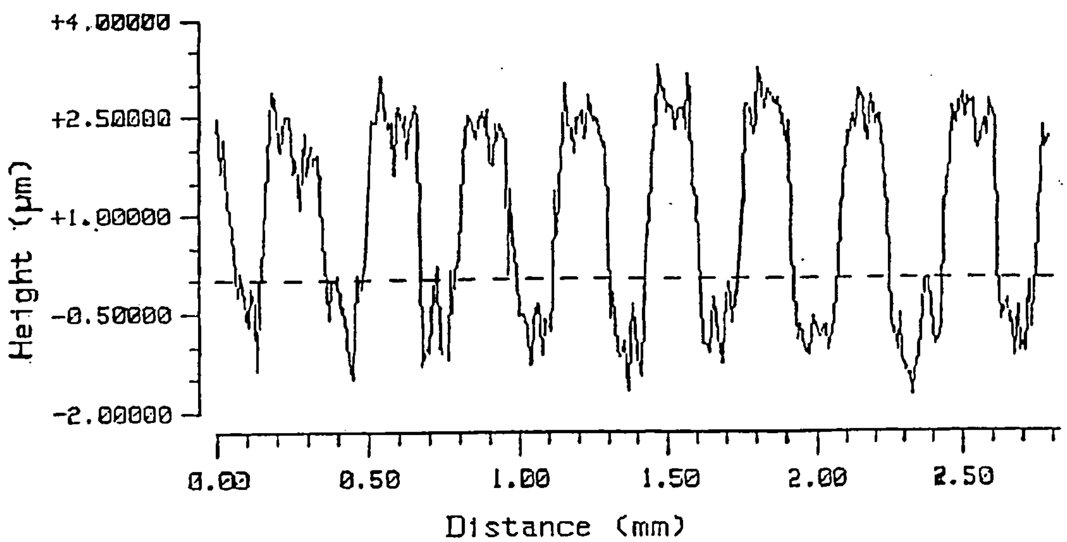
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FIG. 3

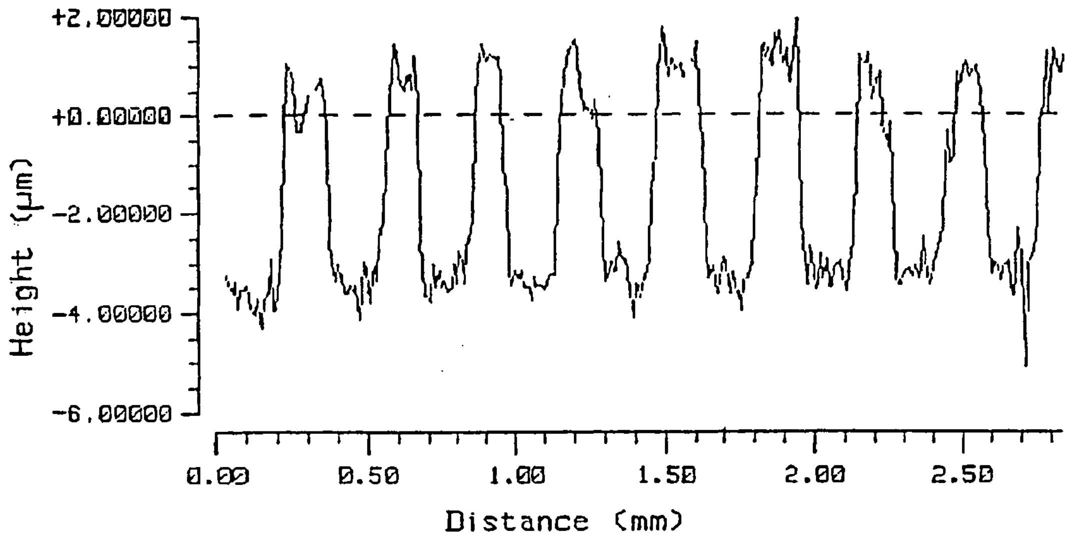
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FIG. 4

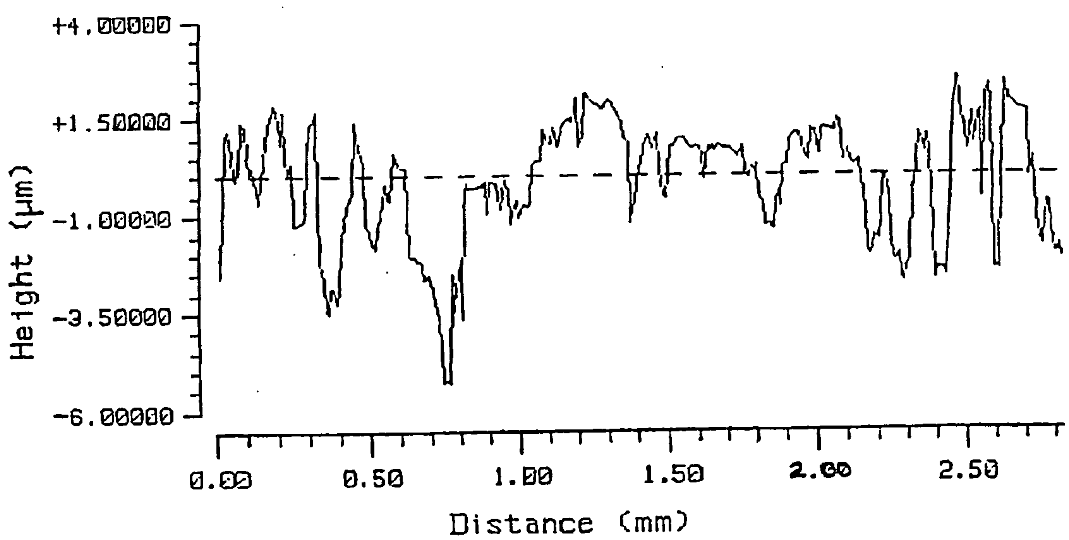
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FIG. 5

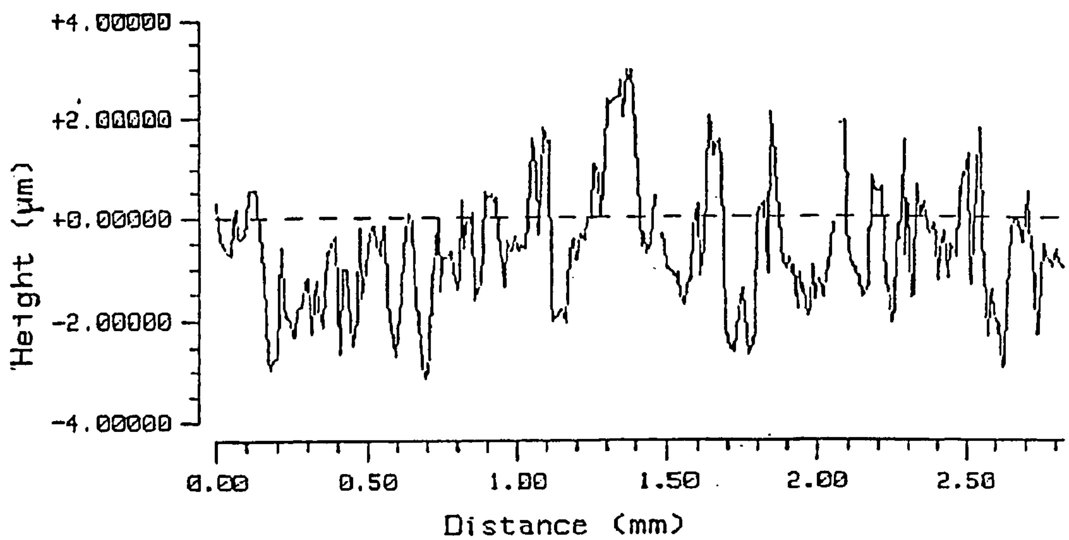
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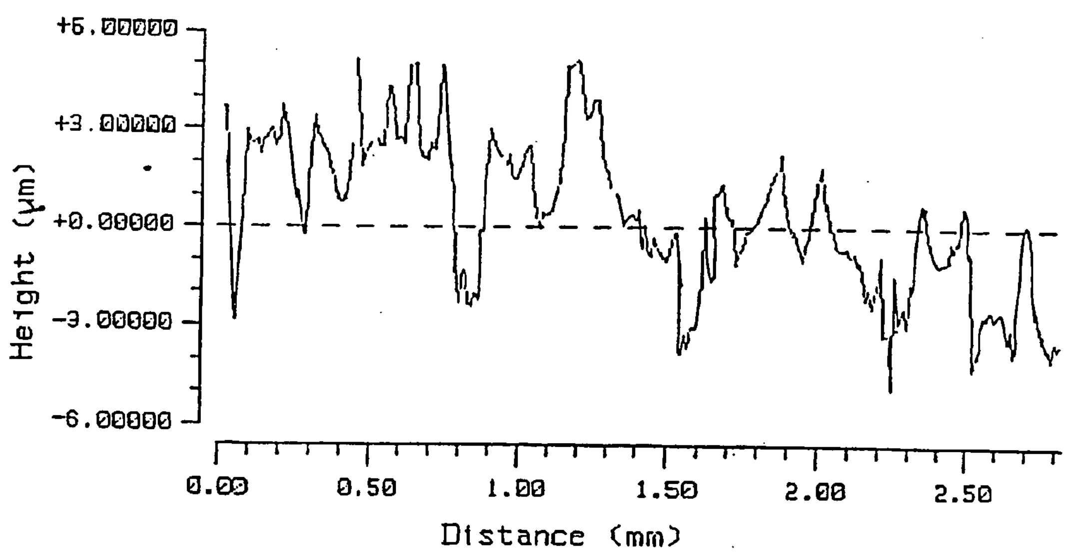
FIG. 6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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 95/00396

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23F1/02 C23F1/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23F C25F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US,A,4 767 489 (LINDNER FREDERICK H) 30 August 1988 see claims; figures ---	1-4,7, 9-11 5
Y	PATENT ABSTRACTS OF JAPAN vol. 010 no. 022 (P-424) ,28 January 1986 & JP,A,60 175050 (NIPPON DENKI KK) 9 September 1985, see abstract; figure ---	5
A	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 15,no. 9, February 1973 NEW YORK, US, pages 2841-2842, ANONYMOUS 'Forming Metallized Patterns on Ceramic Substrates February 1973.' see abstract; figures --- -/--	1-4,7, 10,11

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 338 816 (KAWASAKI STEEL CO) 25 October 1989 see claims; figures	1,6
A	EP,A,0 559 900 (NIPPON STEEL CORP) 15 September 1993 see claims	1,6
A	US,A,4 588 486 (NGUYEN TRUNG H ET AL) 13 May 1986 see claims	8

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 95/00396

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4767489	30-08-88	NONE		
EP-A-0338816	25-10-89	AU-B-	643995	02-12-93
		AU-A-	7739491	08-08-91
		CA-A-	1321625	24-08-93
		DE-D-	68910866	05-01-94
		DE-T-	68910866	17-03-94
		ES-T-	2048283	16-03-94
		JP-A-	2175882	09-07-90
		JP-B-	6051913	06-07-94
		US-A-	4959275	25-09-90
		AU-B-	619279	23-01-92
		AU-A-	3323189	26-10-89
EP-A-0559900	15-09-93	JP-A-	5050118	02-03-93
		CA-A-	2092545	31-01-93
		WO-A-	9303199	18-02-93
		US-A-	5294297	15-03-94
US-A-4588486	13-05-86	DE-A-	3612885	30-10-86
		JP-A-	61242010	28-10-86